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(12) # EUROPEAN PATENT APPLICATION

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(54) **Conductive primers.**

(57) An epoxyester linear block oligomer made with n-1 moles fatty acid units terminated with carboxylic acid groups and n moles of epoxy oligomer, when filled with carbon black, is a particularly effective electrically conductive primer for use over organic-based composites to be electrostatically painted.

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TITLE

Conductive Primers

BACKGROUND

This invention concerns polymers and paints. More particularly it concerns polyester-epoxy polymers filled with carbon black and particularly suited for use as electrically conductive coating compositions for use on automobiles, including non-metallic parts.

The present invention is an adaption of and improvement over that of U.S. application No.613,413 (FF-7795), Huybrechts, Meeus and Timmerman, filed May 24, 1984, the disclosure of which is incorporated herein by reference.

Coating systems for automobiles normally comprise a multiplicity of coatings applied to substrates of steel and sometimes also other materials, including electrically non-conductive organic-based composite materials. Typically, the steel is treated with a phosphate, then a cathodic electrocoat primer is applied. A primer-surfacer is used next to smooth the surface and provide a thick enough coating to permit sanding to a smooth, flat finish. Then a topcoat system is applied, sometimes as a single colored coat, often as a basecoat with solid color or metallic pigments followed by a clear coat.

When a non-conductive material is used for part of a car body, it is important to provide an electrically-conductive coating over it so that when the topcoat paint is applied electrostatically to the entire car, a uniform appearance will be

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produced. Among such non-conductive materials are reaction injection molded (RIM) parts and various fiberglass filled composites.

It is difficult to find a paint that can be made adequately conductive for such applications while still being tough and flexible enough to be a useful paint.

SUMMARY OF THE INVENTION

The present invention provides an electrically conductive coating composition comprising

(a) 5-40% by weight of a block-copolymerized linear oligomer having an average of 3 to 20 mole units of alternating units of

n moles of linear epoxy oligomers terminated with oxirane groups on each end and an $\overline{Mn}$ in the range of 300-5000, and

(n-1) moles of fatty acid units terminated with carboxylic acid groups on each of two ends and having at least 9 carbon atoms,

said linear oligomer being terminated on each end with units of said epoxy oligomers,

(b) 1-20% of a blocked isocyanate which can be unblocked in the coating composition by heating at temperatures not higher than 140°C,

(c) 1-30% of an aminoplast crosslinking agent,

(d) 0-40% by weight of pigment and extenders,

(e) 2-5% by volume based on binder solids of a conductive carbon black, and

(f) 20-80% by weight of organic solvents,

having a specific conductivity measured as a dry, cured film of at least 5.10^{-3} $(\Omega\ cm)^{-1}$.

Coated substrates are also part of the invention.

DETAILED DESCRIPTION

With coating compositions of the invention, the carbon black content was varied and the conductivity of the resulting coating was measured with a "Sprayability Meter" made by Ransburg Electro-Coating Corp. of Indianapolis, Indiana. It was found that at least 2% carbon black by volume based on the total solids was needed to obtain electrostatic sprayability. The following table shows the Ransburg Conductivity rating for various levels of carbon black. A conductivity of at least 100 is needed for a coated substrate to be amenable to electrostatic spraying.

% Carbon Black Volume	Ransburg Conductivity
1	75 (not sprayable)
1.5	75 (not sprayable)
2	145
2.5	165
3	165

Furthermore, the resins of the present invention exhibit substantial toughness, chip resistance and flexibility, making them suitable for use with carbon black fillings as conductive coatings.

In the examples, parts and proportions are given by weight except where indicated otherwise.

EXAMPLE 1

Resin A - Block Epoxy Ester from Epon 1001 and Pripol 1014 - dimer FA

Epon 1001 epoxy resin (Shell)	33.80
Pripol 1014 dimerized fatty acid (Unilever)	16.20
Triethylamine	0.05
Methylisobutyl Ketone (MIBK)	25
heat at reflux (114-116°C) until acid number (AN) = 6-10 visc Q-T (Gardner-Holdt bubble viscosity) at 50% solids in MIBK/CA blend = 1/1	
Cellosolve acetate (CA)	24.95
	100.00

The resulting resin was an oligomer containing 4 moles of $\overline{Mn}$ 900 epoxy and 3 moles of C_{36} dimerized fatty acid, for a total of 7 mole units, end terminated with epoxy.

EXAMPLE 2

Conductive Primer for Coating Bulk Molding Compound, Sheet Molding Compound and Polyamide

Ingredient	Amount	Producer
Grinding stage		
Block epoxy ester of Ex 1	29.73	
Solvesso 150	10.32	Essochem
Bentone 34	0.33	Nat'l Lead
Carbon black XE-2 conductive carbon black	1.11	Phillips Petr.
Xylene	16.69	
Barytes (micronized)	14.49	Sachtleben
Zinc Oxide (American process)	5.04	De Craene
Aluminum silicate pigment	4.23	

Titanium dioxide pigment	11.79	
Guaiacol antioxidant	0.67	Rhone-Poulenc
MPA 60X thixotropic agent	0.67	Baker Caster Oil
Mineral spirits	4.88	Shell
	100.00	

Let down stage

Grind	86.44	
Maprenal MF590 melamine formaldehyde resin	5.85	Hoechst
Xylene	1.00	
Blocked isocyanate ketoxime-blocked aliphatic isocyanate	3.84	Bayer
Ethylene glycol butylether acetate	2.87	
	100.00	

Reduce with Solvesso 150 to spray viscosity of 25-30 sec in Ford cup 4.

The resulting paint was sprayed onto non-conductive automobile parts and provided a tough coating which could be electrostatically sprayed with a topcoat.

CLAIMS

1. An electrically conductive coating composition comprising

(a) 5-40% by weight of a block-copolymerized linear oligomer having an average of 3 to 20 mole units of alternating units of

n moles of linear epoxy oligomers terminated with oxirane groups on each end and an $\overline{Mn}$ in the range of 300-5000, and

(n-1) moles of fatty acid units terminated with carboxylic acid groups on each of two ends and having at least 9 carbon atoms,

said linear oligomer being terminated on each end with units of said epoxy oligomers,

(b) 1-20% of a blocked isocyanate which can be unblocked in the coating composition by heating at temperatures not higher than 140°C,

(c) 1-30% of an aminoplast crosslinking agent,

(d) 0-40% by weight of pigment and extenders,

(e) 2-5% by volume based on binder solids of a conductive carbon black, and

(f) 20-80% by weight of organic solvents,

having a specific conductivity measured as a dry, cured film of at least 5.10^{-3} $(\Omega\,cm)^{-1}$.

2. The coating composition of claim 1 wherein the block epoxy ester is the reaction product of a bisphenol A diepoxy resin with a C_{36}-based aliphatic diacid.

3. The coating composition of claim 1 wherein the blocked isocyanate is a ketoxime-blocked aliphatic isocyanate.

4. The coating composition of claim 1 wherein the crosslinking agent is selected from the group consisting of melamine formaldehyd resins, urea formaldehyde resins and benzoguanamine formaldehyde resins.

5. The coating composition of claim 4 wherein the crosslinking agent is a reactive partially alkylated melamine formaldehyde resin.

6. A coated substrate comprising a substrate of an organic-based composite material coated with a cured coating composition of claim 1, giving an electrical conductivity of at least $5.10^{-3}\,(\Omega\ \mathrm{cm})^{-1}$.

European Patent Office

EUROPEAN SEARCH REPORT

0179281
Application number

EP 85 11 1936

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
A	EP-A-0 024 811 (MOBIL OIL)		C 09 D 5/24 C 08 G 18/42 C 08 G 18/58 C 08 G 18/40 C 09 D 3/58 C 09 D 3/49 C 08 K 3/04
A	US-A-4 380 596 (G.R. WATCHKO)		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 09 D
C 08 G
C 08 K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	21-01-1986	VAN PUYMBROECK M.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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(12) # EUROPEAN PATENT SPECIFICATION

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Background

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The present invention is an adaptation of and improvement over that of U.S. Patent 4,602,053, the disclosure of which is incorporated herein by reference.

Coating systems for automobiles normally comprise a multiplicity of coatings applied to substrates of steel and sometimes also other materials, including electrically non-conductive organic-based composite materials. Typically, the steel is treated with a phosphate, then a cathodic electro-coat primer is applied. A primer-surface is used next to smooth the surface and provide a thick enough coating to permit sanding to a smooth, flat finish. Then a topcoat system is applied, sometimes as a single colored coat, often as a base-coat with solid color or metallic pigments followed by a clear coat.

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(e) 2—5% by volume based on binder solids of a conductive carbon black, and

(f) 20—80% by weight of organic solvents, having a specific conductivity measured as a dry, cured film of at least 5.10^{-3} $(\Omega\ cm)^{-1}$.

Coated substrates are also part of the invention.

A preferred block epoxy ester is the reaction product of a bisphenol A diepoxy resin with a C_{36}-based aliphatic diacid and a preferred blocked isocyanate is a ketoxime-blocked aliphatic isocyanate.

The crosslinking agent is preferably selected from the group consisting of melamine formaldehyde resins, urea formaldehyde resins and benzoguanamine formaldehyde resins. The most preferred crosslinking agent is a reactive partially alkylated melamine formaldehyde resin.

Detailed Description

With coating compositions of the invention, the carbon black content was varied and the conductivity of the resulting coating was measured with a "Sprayability Meter" made by Ransburg Electro-Coating Corp. of Indianapolis, Indiana. It was found that at least 2% carbon black by volume based on the total solids was needed to obtain electrostatic sprayability. The following table shows the Ransburg Conductivity rating for various levels of carbon black. A conductivity of at least 100 is needed for a coated substrate to be amenable to electrostatic spraying.

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Reduce with Solvesso® 150 to spray viscosity of 25—30 sec in Ford cup 4.

The resulting paint was sprayed onto non-conductive automobile parts and provided a tough coating which could be electrostatically sprayed with a topcoat.

Claims

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said linear oligomer being terminated on each end with units of said epoxy oligomers,
(b) 1—20% of a blocked isocyanate which can be unblocked in the coating composition by heating at temperatures not higher than 140°C,
(c) 1—30% of an aminoplast crosslinking agent,
(d) 0—40% by weight of pigment and extenders,
(e) 2—5% by volume based on binder solids of a conductive carbon black, and
(f) 20—80% by weight of organic solvents, having a specific conductivity measured as a dry, cured film of at least 5.10^{-3} $(\Omega\ cm)^{-1}$.

2. The coating composition of claim 1 wherein the block epoxy ester is the reaction product of a bisphenol A diepoxy resin with a C_{36}-based aliphatic diacid.

3. The coating composition of claim 1 wherein the blocked isocyanate is a ketoxime-blocked aliphatic isocyanate.

4. The coating composition of claim 1 wherein the crosslinking agent is selected from the group consisting of melamine formaldehyde resins, urea formaldehyde resins and benzoguanamine formaldehyde resins.

5. The coating composition of claim 4 wherein the crosslinking agent is a reactive partially alkylated melamine formaldehyde resin.

6. A coated substrate comprising a substrate of an organic-based compositie material coated with a cured coating composition of claim 1, giving an electrical conductivity of at least 5.10^{-3} $(\Omega\ cm)^{-1}$.

Patentansprüche

1. Elektrisch leitende Überzugszusammensetzung, welche umfaßt
(a) 5—40 Gew.% eines blockcopolymerisierten linearen Oligomeren mit durchschnittlich 3 bis 20 Mol Einheiten an alternierenden Einheiten von
n-Molen von linearen Epoxyoligomeren, die an jedem Ende mit Oxirangruppen abgeschlossen sind und ein $\overline{Mn}$ im Bereich von 300—5000 aufweisen, und
(n−1)-Molen an Fettsäureeinheiten, die an jedem der beiden Enden mit Carbonsäuregruppen abgeschlossen sind und wenigstens 9 Kohlenstoffatome besitzen,
w bei die linearen Oligomeren an jedem Ende mit Einheiten der genannten Epoxyoligomeren abgeschlossen sind,
(b) 1—20% eines blockierten Isocyanats, das in der Überzugszusammensetzung in den unblockierten Zustand überführt werden kann durch Erhitzen auf Temperaturen nicht höher als 140°C,
(c) 1—30% eines Aminoplastvernetzungsmittels,
(d) 0—40 Gew.-% Pigment und Streckmittel,

(e) 2—5 Volumen-%, bez g n auf den Gehalt an Binderfeststoff n, eines leitfähigen Rußes, und

(f) 20—80 Gew.-% organische Lösungsmittel, und eine spezifische Leitfähigkeit, gemessen an einer trockenen, gehärtet n Folie, von wenigstens $5 \cdot 10^{-3}$ $(\Omega\ cm)^{-1}$ aufweist.

2. Überzugszusammensetzung nach Anspruch 1, bei welcher der Blockepoxyester ein Reaktionsprodukt eines Bisphenol-A-diepoxyharzes mit einer aliphatischen Disäure auf C_{36}-Basis ist.

3. Überzugszusammensetzung nach Anspruch 1, bei der das blockierte Isocyanat ein ketoximblockiertes aliphatisches Isocyanat ist.

4. Überzugszusammensetzung nach Anspruch 1, bei der das Vernetzungsmittel ausgewählt ist aus der Gruppe bestehend aus Melaminformaldehydharzen, Harnstoffformaldehydharzen und Benzoguanaminformaldehydharzen.

5. Überzugszusammensetzung nach Anspruch 4, bei der das Vernetzungsmittel ein reaktives, teilweise alkyliertes Melaminformaldehydharz ist.

6. Überzogenes Substrat, umfassend ein Substrat aus einem Verbundmaterial auf organischer Basis, das mit einer gehärteten Zusammensetzung nach Anspruch 1 überzogen ist und eine elektrische Leitfähigkeit von wenigstens $5 \cdot 10^{-3}$ $(\Omega\ cm)^{-1}$ ergibt.

Revendications

1. Une composition de revêtement électriquement conducteur, comprenant

(a) 5 à 40% en poids d'un oligmère linéaire copolymérisé en séquences comptant en moyenne 3 à 20 unités molaires de motifs alternés de

n moles d'oligomères époxydes linéaires terminés à chaque extrémité par des groupes oxiranne et dont le $\overline{Mn}$ est compris dans l'intervalle de 300 à 5000, et

(n−1) moles de motifs acide gras terminés à chacune des deux extrémités par des groupes acide carboxylique et comptant au moins 9 atomes de carbone,

ledit oligomère linéaire étant terminé à chaque extrémité par des motifs desdits oligomères époxydes,

(b) 1 à 20% d'un iosocyanate bloqué qui peut être débloqué dans la composition de revêtement par chauffage à des températures non supérieures à 140°C,

(c) 1 à 30% d'un agent réticulateur aminoplaste,

(d) 0 à 40% en poids de pigment et de charges inertes,

(e) 2 à 5% en volume, sure la base des solides liants, d'un noir de carbone conducteur, et

(f) 20 à 80% en poids de solvants organiques, ayant une conductivité spécifique, measurée à l'état de pellicule durcie sèche, d'au moins $5 \cdot 10^{-3}$ $(\Omega\ cm)^{-1}$.

2. La composition de revêtement de la revendication 1, dans laquelle l'ester époxyde séquencé est le produit de réaction d'une résine diépoxyde de bisphénol A avec un diacide aliphatique en C_{36}.

3. La composition de revêtement de la revendication 1, dans laquelle l'isocyanate bloqué est un isocyanate aliphatique bloqué par une cétoxime.

4. La composition de revêtement de la revendication 1, dans laquelle l'agent réticulateur est choisi dans le groupe formé par les résines mélamine-formaldehyde, les résines urée-formaldéhyde et les résines benzoguanamineformaldéhyde.

5. La composition de revêtement de la revendication 4, dans laquelle l'agent réticulateur est une résine mélamine-formaldéhyde réactive partiellement alkylée.

6. Un substrat revête comprenant un substrat en un matériau composite à base organique revêtu par une composition de revêtement durcie de la revendication 1, présentant une conductivité électrique d'au moins $5 \cdot 10^{-3}$ $(\Omega\ cm)^{-1}$.